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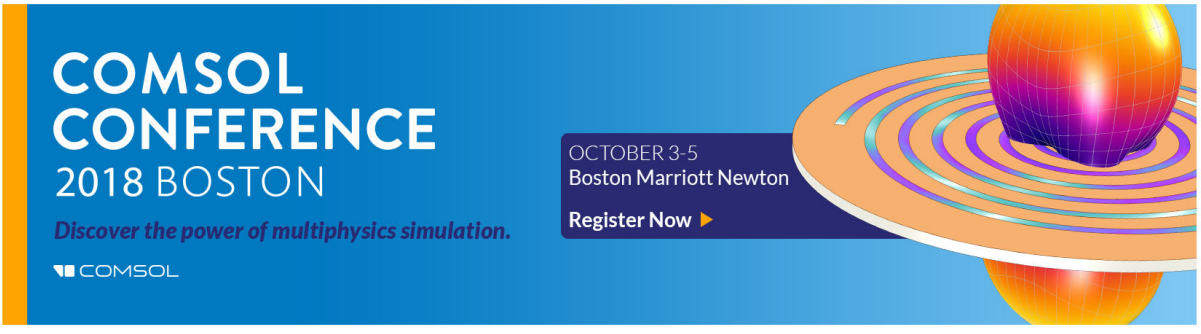

Spectroscopic study of conformational dynamics of 1,1′-binaphthyl in a jet

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Analysis of the fluorescence excitation spectrum of 1,1′-binaphthyl in a jet shows that in the origin region there are four transitions, in an energy range of 150 cm^{-1}, which strongly overlap through the occurrence of strong progressions in a torsional mode. The four transitions can be described in terms of excitations to levels of an interchange-equivalent naphthalene dimer in a *trans* and *cis* configuration. The dimer splittings are 50 and 63 cm^{-1} for 1,1′-binaphthyl-h_{14} and 50 and 57 cm^{-1} for 1,1′-binaphthyl-d_{14}. The Franck–Condon envelope of the librational progressions indicates that the potential energy surface for states of *A* and *B* symmetry are different, which implies that the interplanar angle in each of the four excited states is different. From the intensities in the *A* and *B* progressions it is further deduced that for the origin transitions the transition moment in each subunit is oriented in the naphthalene plane at an angle of $\sim 50°$ with respect to the long axis. From the Franck–Condon envelope in the librational progressions it is further deduced that the change in torsional angle on optical excitation to the *B*-potential energy surface is $\sim 12°$ to the *trans* and 6° to the *cis* side. From this a maximum (state dependent) barrier of 150 cm^{-1} is calculated. It is further shown that, near the intense false origin, numerous modes appear which are induced through vibrational mixing. This Fermi-resonance effect is most obvious in perdeutero binaphthyl, where the vibronically induced intensity in the region of the most intense false origin is smeared out over many modes. The emission spectrum of the molecule can be interpreted by assuming that in 1,1′-binaphthyl very efficient vibrational relaxation occurs through conversion of vibrational into librational energy with molecular rotations providing the matching energy. It is also suggested that, after vibronic excitation, vibrational relaxation occurs into the energetically most stable structure. Finally, the observed red shift of the binaphthyl fluorescence in solution must be due to solvent stabilization of the excited molecule in a structure which is more planar than the one observed in the isolated molecule.

I. INTRODUCTION

Aromatic molecules composed of two planar aromatic systems joined by a single carbon–carbon bond are flexible in the sense that the molecular conformation is very sensitive to perturbations from the environment. A classical example is the biphenyl molecule which in the solid state is planar[1] while in the gas phase the molecule occurs in a twisted structure with an angle between the rings of 42°.[2] On optical excitation to the lowest electronic state the molecule becomes (nearly) planar again.[3] A necessary consequence of this structural lability is that the optical spectrum of such molecules critically depends on the surroundings, which may stabilize the molecule in a structure which in the free molecule is not the energetically lowest one. In the case that the resulting molecular structure is such that the aromatic ring systems are orthogonal to one another, leading to a minimal interaction between the systems, the optical spectrum will look like a slightly perturbed version of the sum spectrum of the individual chromophores. In the other limit, where the aromatic rings are (nearly) coplanar, the electronic excitations will not be localized on either of the two halves and consequently the optical spectrum will bear no resemblance to the spectrum of either chromomphore. The binaphtyls form a series of molecules that show the former behavior. In 1,1′-binaphthyl the optical spectrum in solution resembles very much that of naphthalene, as first noted by Friedel and Orchin,[4] suggesting that in this case the naphthalene rings are nearly perpendicular. This seems to imply that the ground-state conformation is mainly determined by intramolecular hydrogen–hydrogen repulsion which near 90° is at a minimum.

In 2,2′-binaphthyl the optical spectrum is less naphthalenic and shifted to the red, in agreement with less steric hindrance of a planar conformation. In 1,2′-binaphthyl an intermediate situation exists and the spectrum of this molecule indeed falls in between that of the other species.[4]

Of these three binaphthyls, 1,1′-binaphthyl (BN from here on) is the most studied one. In an early optical study of BN in the condensed phase by Hochstrasser[5] it was proposed that the ground state potential surface exhibits one minimum for a "*cis*-inclined" (near 68°) conformation, while the excited state potential for twisting the molecule around the connecting C–C′ bond has a double minimum with a barrier height, in alcoholic solution, of less than 500 cm^{-1}. Furthermore it was suggested that in the excited state the *trans* structure is the more stable one. A drawing of the molecule, in a "*cis*-oid" form, and an artist's impression of the potential energy surface for the ground and excited electronic state of BN is given in Fig. 1. Post *et al.*[6] have also made a study of the absorption and emission spectrum of BN in liquid and solid environment at higher optical resolution. They interpreted an observed 4000 cm^{-1} red shift of the emission in solution to a change in molecular geometry of BN from an initially orthogonal to a more planar structure. In a solid

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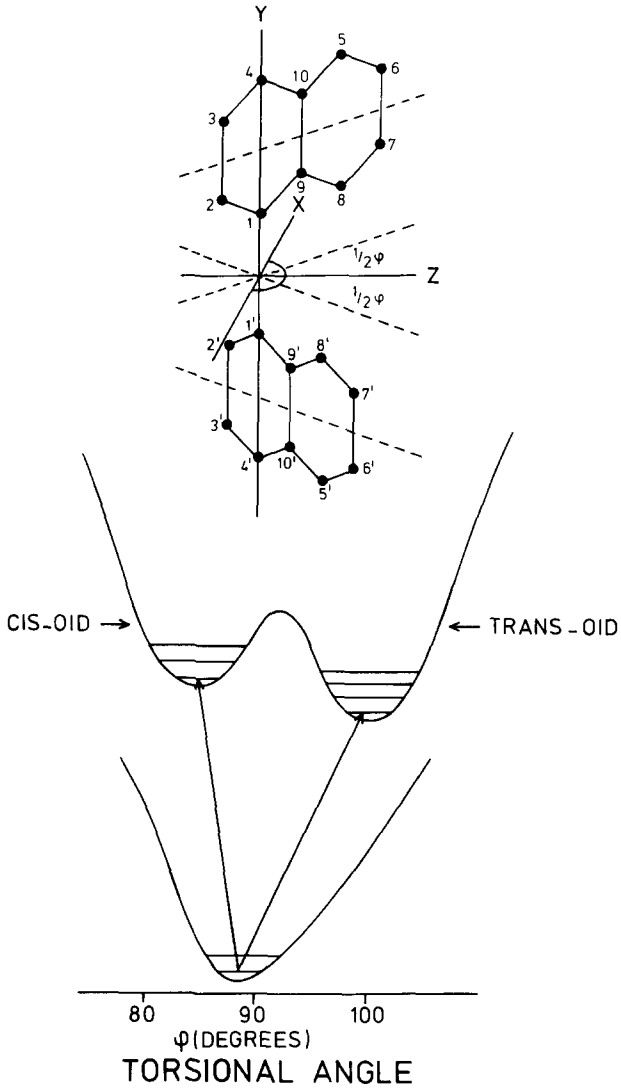

FIG. 1. Structure of 1,1'-binaphthyl and an "artist's" impression of the potential energy surface in the ground and excited (A symmetry) state of the molecule along the torsional coordinate.

solution of BN they observed only an emission spectrum that closely resembled that of naphthalene. The interpretation given of these observations is that, in a solid, the excited state structure is frozen in the ground state conformation in which the naphthalene rings are nearly perpendicular to one another. In a liquid environment rotations around the interconnecting C–C' bond are possible and an energetically more favorable planar structure can be reached after optical excitation. Shank *et al.*[7] have tried to obtain information on the conformational dynamics of BN is solution using picosecond pulse-probe techniques. From this study it was concluded that after optical excitation to the lowest excited singlet state a 2.5 ps relaxation process occurs. Whether this relaxation process was connected with excited state isomerization of the molecule could not be established. In a recent study by Riley *et al.*[8] the emission of BN was studied in an *n*-pentane matrix at low temperature. In this study, emission from two different BN conformers was observed. The energetically higher emission resembled very much the spectrum of naphthalene, while the other was of completely different appearance. Riley *et al.*[8] interpreted these observations by assuming that in the cooling process they had frozen two different BN conformers, one with a conformation with nearly orthogonal rings and another which is more planar. This experiment therefore suggests that, in solution, BN also may occur in two different ground state conformations. In view of the interesting conformational dynamics that BN exhibits in condensed phases, it seemed pertinent to study this molecule under isolated conditions in the gas phase.

We have recently reported the results of a preliminary optical study of jet-cooled BN.[9] An important conclusion of that work was that the optical spectrum of BN looks very much like that of a naphthalene dimer and that the molecule in the ground and excited state adopts a conformation in which the naphthalene rings are nearly perpendicular. An additional suggestion, made on the basis of the observed emission spectrum of BN in a jet, was that very fast vibrational relaxation occurs through conversion of vibrational into librational (torsional) energy.

In this paper we report results of additional optical experiments on perproto and perdeutero BN in a jet which lead to a different interpretation of the spectrum. The most important new conclusion is that the excited state potential energy surface contains a double minimum with a barrier between conformations which is very low, most likely less than 200 cm^{-1}. A further conclusion is that the transition moment in the naphthalene subunit of BN makes an angle of $\sim 50°$ with the long axis in naphthalene. The vibronic absorption spectrum of BN is also presented and compared to the corresponding spectrum of naphthalene. It is suggested that many of the low-frequency modes near the strong "false" origin are induced by vibrational mixing with this coupling mode. In perdeutero BN this leads to a very complex structure in the region of the most active vibronic coupling mode. The previously made suggestion that vibrational relaxation in BN proceeds via conversion of vibrational into librational energy is confirmed. Finally the relevance of these results to the interpretation of the solution dynamics of BN is discussed and new experiments are suggested.

II. EXPERIMENTAL

The supersonic beam was generated by expanding helium (stagnation pressure between 0.3 and 6 bar) seeded with 1,1'-binaphthyl through a 1 mm diameter nozzle pulsed at 10 to 20 Hz. The expansion chamber was pumped by an Edwards 18B3 vapor booster, backed by an Edwards ES4000 single-stage rotary pump. The background pressure during the experiments was around 10^{-2} Torr. The laser crossed the beam between 0.5 and 6 cm downstream from the nozzle. The 1,1'-binaphthyl had to be heated to about 100–150 °C in order to get sufficient vapor pressure. The fluorescence excitation spectra were obtained using a frequency-doubled Molectron DL14P dye laser (bandwidth 0.3 cm^{-1}) pumped by a Molectron UV22 nitrogen laser. Fluorescence spectra were taken using either the nitrogen laser or a Lambda Physik EMG101 excimer laser, operating at 308 nm, as a pump source for the dye laser and a 3/4 m SPEX 1702 monochromator as dispersive element. Fluorescence lifetimes were determined by using a PAR model 162 Boxcar integrator equipped with a model 165 plug-in unit or

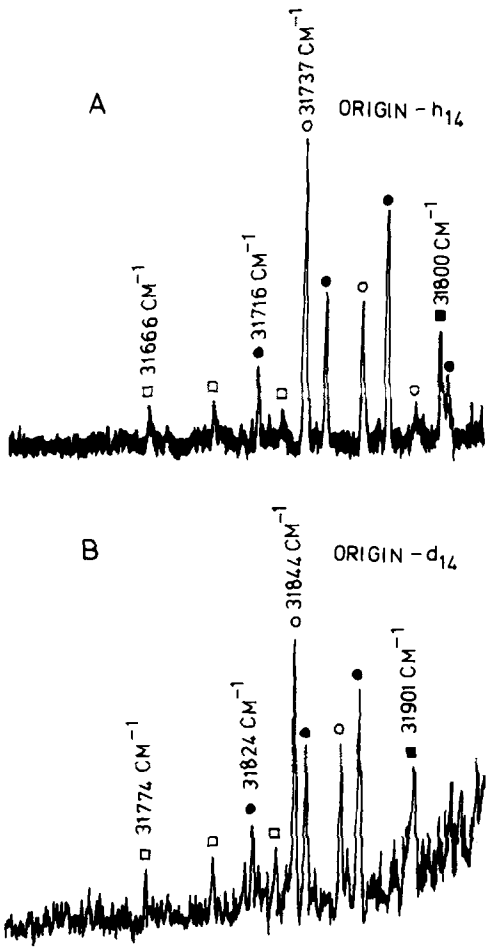

FIG. 2. Fluorescence excitation spectra of 1,1'-binaphthyl-h_{14} (A) and -d_{14} (*B*) in the region of the origin. The indicated line positions locate the four origins in this region. The different librational progressions have been indicated by open squares, solid squares, open circles, and solid circles.

by direct observation on a Tektronix R7912 transient digitizer. 1,1'-Binaphthyl was obtained from Kodak and purified by repeated sublimation. Perdeuterated 1,1'-binaphthyl was prepared from 1-bromonaphthalene-d_7, via a synthetic route described by Taylor *et al.*[10] Purification of the product was achieved chromatographically using an aluminium oxide column and hexane as an eluent.

III. RESULTS AND DISCUSSION

A. Origin spectrum

Figure 2 presents the fluorescence excitation spectra of jet-cooled BN-h_{14} and -d_{14} in the origin region. Comparison of the two spectra shows that each is composed of two strong and two weak overlapping progressions in modes of low frequency ($\sim$30 cm^{-1}). The position of each of the lines observed in the progressions is given in Table I. In the spectrum of BN-h_{14} the (observed) origins of these progressions occur at 31 666, 31 716, 31 737, and 31 800 cm^{-1}. The shift of the center of these origins with respect to the origin of the gas phase naphthalene absorption[11] is only 290 cm^{-1} suggesting that the naphthalene rings in binaphthyl only weakly interact. This is also confirmed by the average measured shift of these origins on deuteration which is 106 cm^{-1}, in excellent agreement with the expected shift of 108 cm^{-1} for an α-substituted naphthalene molecule.[12] It seems appropriate then, as was done in a preliminary report on the BN spectrum,[9] to try and explain the absorption spectrum of BN in terms of a weakly coupled dimer. This dimer exhibits a C_2 axis of symmetry and therefore all states of the dimer should be classified as either symmetric (*A*) or antisymmetric (*B*) with respect to this symmetry axis. Consequently each single absorption line in the naphthalene monomer is split in two by the interchange equivalent interaction between the rings. We therefore expect each binaphthyl conformation to exhibit two groups of lines, with relative intensities determined by the relative orientation of the transition moments in each naphthalene ring. The observation of *four* different absorption origins then indicates the occurrence of two different binaphthyl conformations in the excited state; most likely one in a "*cis*-" the other in a "*trans*-oid" configuration.

Prior to a further discussion of the spectrum we wish to point out that the weak lines in the spectrum of Fig. 2 can not be assigned to hot bands associated with the strong lines as was done in our preliminary report of the spectrum. The main and decisive argument against such an analysis comes from study of the origin spectrum of BN-d_{14} which shows that the librational frequencies in the weak progression have remained unchanged, in contrast to the librational frequencies in the intense progressions which show an appreciable deuteration effect. Also their interpretation as arising from a helium complex of BN can be excluded by study of the vibronic spectra, which show no similar features. All the lines observed in the origin region then must be due to transitions in cold BN molecules which are excited to a *cis*- and *trans*-like structure.

Proceeding now with the analysis of the optical spectrum of BN we first have to answer the questions which of the four observed progressions belong to one conformation and how are the resulting two pairs matched to absorption to the *cis* and *trans* forms of BN in the excited state. The decisive consideration in this choice must be that the combined integrated intensity in the plus and minus dimer states should be the same for absorption to the *cis* and *trans* conformation. Consequently one of the weak progressions must belong to one of the strong ones, leaving a second set of a strong and weak progression. Note that indeed the integrated intensities in both these sets are, within error limits, identical. A careful look at the Franck–Condon envelope in all progressions also shows that again they fall into two sets, one in which the origins are the most intense members of the progression (O_3 and O_4) and one (O_1 and O_2) where most of the intensity in the progression resides in higher quantum number excitations (O_1 and O_2). A more quantatative interpretation of this intensity distribution is given in Sec. III C, but qualitatively we conclude that for one conformation the change in interplanar angle on optical excitation is much larger than for the other, as might be expected. We therefore conclude that O_1 and O_2 are the *A* and *B* levels [*vide infra*, see Eq. (1)] of BN in one conformation, named T hereafter, and that O_3 and O_4 are the *B* and *A* levels in the other conformation, named C from here on. With this analysis we conclude that in the T conformation the dimer splitting is 50 cm^{-1} and in the C conformation it is 63 cm^{-1}. For perdeutero BN

TABLE I. Spectral line positions (in cm^{-1}) of 1,1'-binaphthyl in the origin region and of selected vibronic transitions. The absolute accuracy in line position is $\pm 3\ cm^{-1}$, the relative accuracy in the origin region is $\pm \frac{1}{2}$ cm^{-1}.

31 666	$O_1(A)$	31 774	$O_1(A)$
31 696	$O_1 + 30$	31 805	$0_1 + 31$
31 716	$O_2(B)$	31 824	$O_2(B)$
31 726	$O_1 + 2\times30$	31 835	$O_1 + 31 + 30$
31 737	$O_3(B)$	31 844	$O_3(B)$
31 746	$O_2 + 30$	31 850	$O_2 + 26$
31 765	$O_3 + 28$	31 866	$O_3 + 22$
31 775	$O_2 + 30 + 29$	31 875	$O_2 + 26 + 25$
31 792	$O_3 + 28 + 27$	...	
31 800	$O_4(A)$	31 901	$O_4(A)$
31 803	$O_2 + 30 + 29 + 28$	...	
31 909	T + 218	32 005	T + 206
31 978	C + 209	32 065	T + 266
32 010	T + 319	32 127	C + 254
32 036	C + 267	32 159	T + 360
32 072	C + 303		
32 122	T + 431	~32 223	T + 424
32 159	C + 390	~32 254	C + 381
32 169	C + 400		
32 221	C + 452		
32 243	T + 552		
32 557	C + 788	32 658	C + 785
32 576	T + 885	32 766	T + 967
32 785	T + 1094	32 792	T + 993
32 901	C + 1132	32 855	T + 1161
33 134	C + 1365	32 957	C + 1084
33 288	C + 1519		
33 292	T + 1601		

[a] T and C here refer to the position of the center of $O_1 + O_2$ and of $O_3 + O_4$, respectively.
[b] Position of first moment of molecular vibronic eigenstates (see the text, Sec. III B).

these numbers are 50 and 57 cm^{-1} respectively. The gap between the center of these dimer states is 77.5 cm^{-1} (73.5 cm^{-1} for BN-d_{14}) which should be interpreted as the difference in site shift of the substituted naphthalene molecule when the substituent is either the *cis* or *trans* position with respect to the naphthalene ring. It is further very interesting to note that, while the dimer splitting for both conformations is quite comparable, the positions of the A and B levels are inverted, in agreement with theoretical calculations by Post *et al.*[13]

We now turn to a discussion of the relative intensities of the A and B progressions. In a dimer model of BN these relative intensities should directly relate to the angle between the transition dipole in each naphthalene subunit. While in the isolated naphthalene molecule the transition dipole, for the lowest singlet transition, is aligned along the long axis of the molecule, in a substituted naphthalene this no longer need be the case. In fact the reduction in symmetry of the naphthalene subunit in BN, caused by C–C' bonding to another naphthalene, will induce mixing between the weakly allowed lowest and strongly allowed (and short axis polarized) second excited singlet state in naphthalene, thereby also inducing a transition dipole component along the short axis of the naphthalene molecule. Taking this fact into account we come to the following relation for the relative integrated intensities in the progressions of A and B symmetry in a dimer description of BN:

$$\frac{I_A}{I_B} = \frac{(1 + \cos\varphi_A)}{(1 - \cos\varphi_B) + 2\gamma^2}. \tag{1}$$

Here φ is the interplanar angle between the naphthalene rings in the excited state, for either the C or T structure, and $\gamma = \mu_M/\mu_L$ is the ratio between the transition dipole components along the short and long axes of naphthalene. In the usual dimer model the angle φ should be identical for both dimer levels. In Sec. III C we will show that there is evidence that this angle is different for the different dimer states of BN, a possibility which has been included in Eq. (1). However, even in case $\varphi_A = \varphi_B$ we can not derive information from the spectrum on the structure of BN in the C and T forms without knowledge of γ. In Sec. III C we will show, that with a reasonable assumption about the ground state conformation of BN, an averaged value for γ of ~ 1.2 will be derived which implies that the transition dipole in each subunit is aligned in the naphthalene plane at an angle of about 50° with respect to the long axis. Such a value of γ further implies that over half of the intensity in the origin region of BN is induced by configurational mixing through the loss of symmetry of the naphthalene molecular unit.

We finally wish to address the question of which conformation of BN belongs to the observed dimer splittings. Again, *a priori*, no choice can be made unless the ground state conformation be known. If the ground state conformation is *cis*-like, as follows from a molecular mechanics calculation,[14] then, from the Franck–Condon pattern in the librational progression it is clear that the dimer absorbing at lower energy belongs to the *trans* configuration. It is tempting then to assign the BN species with the largest dimer splitting to the *cis*-inclined (C) species in agreement with the notion that in the more *cis*-inclined form the orbital overlap between the naphthalene rings is larger, which would lead to a larger interchange interaction between the naphthalene

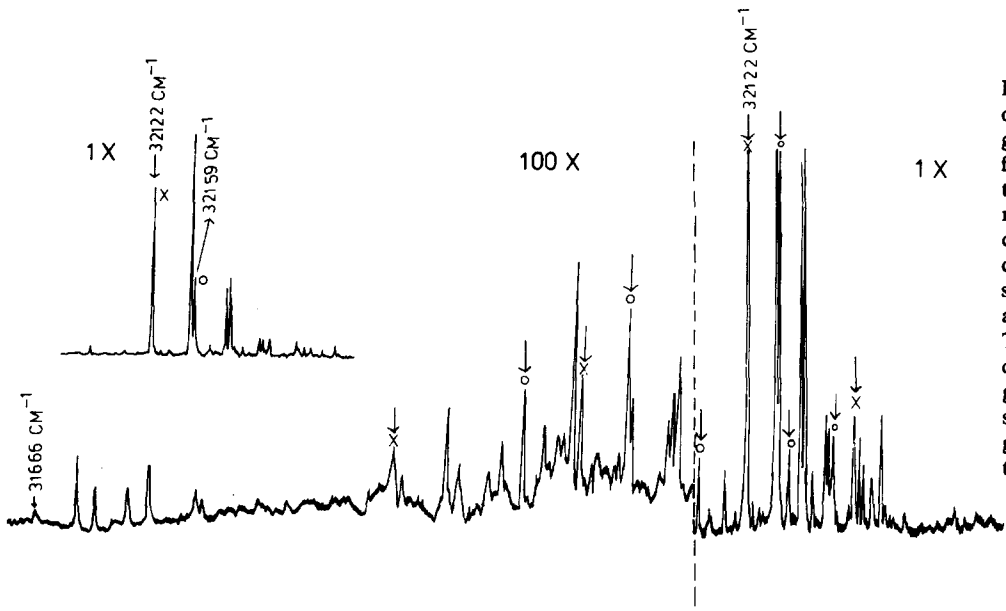

FIG. 3. Fluorescence excitation spectrum of 1,1'-binaphthyl-h_{14} from the origin region up to the region of the most intense false origin. Note that in the origin region the weak progression, shown in Fig. 2, is missing. This is due to the fact that the frequency doubling crystal is manually tuned during a scan of the spectrum. The insert shows the spectrum of the false origin again at lower photomultiplier setting. The arrows in the figure mark the position of the initial member of a librational progression. The open (A) and cross (B) circle symbols indicate to which potential energy surface, of A or B symmetry, the librational progression belongs.

molecules. We therefore opt for this assignment which assumes the ground state of BN to be most stable in a *cis*-inclined form with an interplanar angle close to 90°.

B. Vibronic spectra

In Figs. 3 and 4 we display the fluorescence excitation spectra of BN-h_{14} up to $\sim 1700\ \text{cm}^{-1}$ excess vibrational energy. As in the origin region we observe overlapping spectra which are complicated by the librational progressions. Two different type librational progressions are encountered with frequencies close to the ones observed in the origin region. Arrows in the spectra indicate the position of the first member of a librational progression and the star and open circle symbols indicate the different librational progressions observed. Figure 5 finally shows the most intense group of lines in the perdeutero BN spectrum. The rest of the spectrum of this molecule is not shown but can easily be correlated with the spectrum of the perproto species. Table I contains the line positions of all lines in the region of the origin and most intense false origin for both perproto and perdeutero 1,1'-BN and the line positions of the initial members of the other vibronic transitions.

When we now turn to a discussion of the vibronic spectrum of BN-h_{14} we first note that the vibronic intensity in the region of $\sim$ 400 cm^{-1} excess vibrational energy, as measured from the center of all origins at 31 730 cm^{-1}, exceeds the origin intensity by a factor of at least 100. Note further that half of the pure electronic origin intensity is polarized perpendicular to the C_2 axis of the molecule. In our previous letter[9] we already concluded that this group of lines must be the region of the false origin of binaphthyl related to the 435 cm^{-1} (b_{1g}) vibronic origin in the $^1B_{3u} \leftarrow {}^1A_{1g}$ spectrum of naphthalene.[15] In the naphthalene spectrum the intensity ratio between the false and true origin absorptions is about 50[11] indicating that vibronic coupling is more effective in BN. This is due to the fact that the gap between the "borrowing" and "lending" states is reduced from $\sim 4000\ \text{cm}^{-1}$ in naphthalene to $\sim 2500\ \text{cm}^{-1}$ in BN.[6] In a very simple picture one can say that the interchange coupling between the $B_{2u} \leftarrow A_{1g}$ transitions in BN, splits the single transition of naphthalene into A and B components. According to the calculations of Post *et al.*,[13] the B component is at lower energy. The mean of these exciton components will further undergo a dispersion shift due to the presence of a polarizable ground state napththalene next to an excited napthalene molecule. This site shift will exceed that of the lowest transition, resulting in a reduced gap between the B component (polarized parallel to the interconnecting C–C' bond) of the second naphthalene-like singlet state and the lowest BN transition, compared to the gap between the corresponding transitions in naphthalene.

Comparison of the librational frequencies in this false origin with the ones in the origin region initially suggests[9] that the first strong line at 32 122 cm^{-1} must be interpreted as a 406 cm^{-1} vibrational addition to the origin (O_2) at 31 716 cm^{-1}, with the line at 32 159 cm^{-1} assigned to a 422 cm^{-1} mode built on second B-type origin (O_3) at 31 737

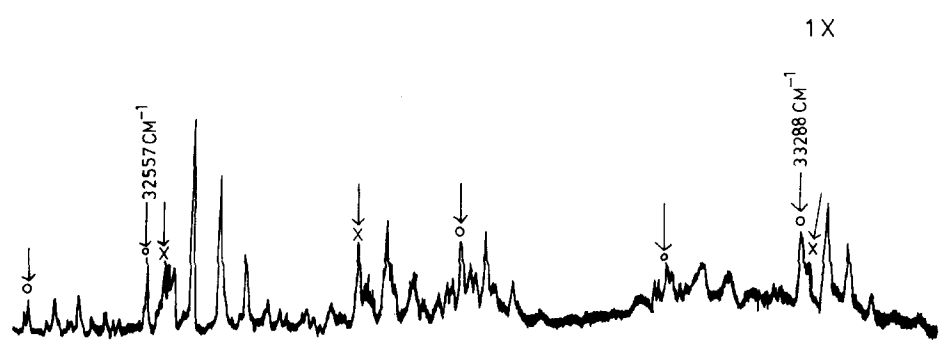

FIG. 4. Continuation of the fluorescence excitation spectrum of 1,1'-binaphthyl-h_{14} up to 1700 cm^{-1} excess vibrational energy. For an explanation of the symbols consult the caption of Fig. 3.

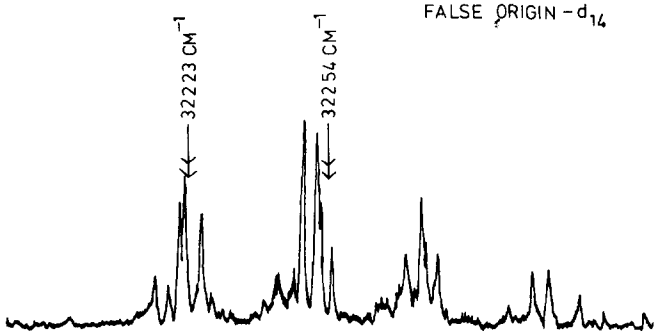

FIG. 5. Fluorescence excitation spectrum of the false origin in 1,1'-binaphthyl-d_{14}. For an explanation of the complicated structure in this region consult the text. The double headed arrows in this figure indicate the positions of "unperturbed" vibronic transitions in the molecule.

cm^{-1}. Along the same lines it seems attractive to assign a librational progression starting at 32 072 cm^{-1} to a 406 cm^{-1} vibrational addition to the A-symmetry (O_1) origin at 31 666 cm^{-1} and a weak progression starting at 32 223 cm^{-1} to a 423 cm^{-1} mode built on the origin (O_4) at 31 800 cm^{-1}. There are two major problems with the latter two assignments. The first one recognizes the fact that the librational frequency in the librational progression based on this 406 cm^{-1} mode is 28 cm^{-1} while in the origin the corresponding frequency is 30 cm^{-1}. Purely on the basis of this librational-frequency argument this series of lines must be assigned to a 335 cm^{-1} mode based on the B-dimer origin at 31 737 cm^{-1}. We note that a similar alternative interpretation exists for the librational progression starting at 32 223 cm^{-1}. The second problem concerns the fact that in the spectrum of the perdeutero BN molecule no corresponding mode, $\sim$400 cm^{-1} from the origin at 31 774 cm^{-1}, could be identified. Together these points lead us to conclude that in the perproto spectrum no lines in the vibronic region can unequivocally be assigned to the weak origins of A spatial symmetry.

We therefore conclude that these vibronic transitions are all short-axis polarized transitions induced by a b_{1g} type mode that, at each naphthalene moiety, couples the second excited singlet state (short-axis polarized) into the lowest one. These vibronic transitions are therefore described by the out-of-phase (B) combination of local vibronic transitions, this is the so-called weak coupling limit.[16] In this weak coupling limit it is further easily established that the dimer splitting of these vibronically induced bands is determined by the dimer splitting of the state from which the intensity is borrowed and is quite often negligible as was shown to be the case for the b_{1g} mode in a naphthalene crystal.[17] Assuming therefore that the dimer splitting in the false origin of BN is negligible, the upper state vibrational frequencies should be calculated with regard to the mean of the position of the dimer levels in the origin region. We then find for the b_{1g} type excited state mode in BN for the *trans* conformation 431 cm^{-1} and for the *cis* 390 cm^{-1}. The reduction of the average frequency (411 cm^{-1}) of the coupling mode compared to the corresponding mode in naphthalene (435 cm^{-1}) is due to the aforementioned smaller gap between the interacting states. A further remarkable point of the spectrum in the region of the false origin is that the intensity distribution in the librational progression is rather different from what is observed in the origin, while the observed librational frequencies are identical. The important difference between the pure electronic transition and the b_{1g}-type vibronic transition, as we just pointed out, is the magnitude of the coupling between the excitations. The observed drastic effect of vibrational excitation on the librational Franck–Condon envelope therefore points to a small barrier for rotation of a naphthalene ring from a *cis* to a *trans*oid position. In the next section we will show that a barrier of up to only 200 cm^{-1} is compatible with the results. We now continue with a discussion of the other vibronic features observed in the excitation spectrum of BN. In the region between the false and the true origins, as Fig. 3 shows, a number of weak lines appear, the intensities of which seem to be inversely correlated to the frequency difference with the false origin. We suggest that these lines are spectroscopically observable through intermode mixing with the b_{1g} type modes that induce the intense false origins in the BN spectrum. On the high frequency side some lines are observed which are also interpreted as arising from Fermi-resonance effects. In order to explain the intensities of these lines we have to assume that the intermode coupling of the inducing modes with the induced ones is on the order of 10 cm^{-1}. We have not attempted to assign all these modes to BN fundamentals or overtones but wish to note that the Raman spectrum of BN-h_{14}[8] contains several low frequency modes which could be the corresponding ground state partners.

It is more easy to correlate the vibronic intensity at higher energy and we clearly observe the counterpart of the 910 cm^{-1} mode in the naphthalene spectrum in BN-h_{14} at 788 and 885 cm^{-1}. Again the drop in average frequency of this coupling mode must be related to the smaller gap between the interacting states in BN. In the region of 1100 cm^{-1} excess vibrational energy we also clearly recognize two vibrational progressions which can be related to the 1135 cm^{-1} combination mode in the naphthalene spectrum.

In the spectrum of perdeutero BN we clearly recognize absorption features similar to the spectrum of the perproto molecule except for the region of the false origin, shown in Fig. 5, which looks extremely complex. By comparing this spectrum with the one for BN-h_{14}, displayed in Fig. 3, we note that each line in the spectrum of the perdeutero compound in this region is split into at least three and possibly five components. The second group of lines in this spectrum looks even more complex, which is not surprising as the corresponding "line" in the spectrum of the perproto species is also doubled. From the previous discussion on the intensities of the weak lines surrounding the false origin it is clear what has happened. Some of the modes, which in the perproto molecule were at higher frequency than the coupling mode and were induced in the spectrum by intermode mixing, have on deuteration become near degenerate with it, resulting in a severe mixing of these modes. We therefore ascribe the complexity of the spectrum in this region to Fermi-resonance effects. This interpretation is in line with the observation that, at higher excess vibrational energy, the spectrum does not exhibit this complexity.

In order to calculate from this "molecular eigenstate spectrum" the unperturbed frequency of the coupling mode,

the first moment of each relevant group of lines must be taken. This results in a zero-order frequency for the coupling mode, based on the center of the origin absorptions for the *trans* configuration of 424 cm^{-1} and for the *cis* one 381 cm^{-1}. The reduction, on deuteration, of the average frequency of the coupling mode in BN from 411 to 403 cm^{-1} is very similar to what is observed for naphthalene itself, where, on deuteration, the b_{1g} mode drops from 435 to 418 cm^{-1}.[15]

C. Torsional modes of 1,1'-binaphthyl

Throughout the absorption spectrum of BN slightly anharmonic progressions in low frequency modes are observed. In BN-h_{14} modes of 30, 30, and 28 cm^{-1} are found while in BN-d_{14} modes of 30, 26, and 22 cm^{-1} are observed. These low frequency modes are most likely connected with torsional (librational) motions of the naphthalene rings around the interconnecting C–C' bond. Similar type torsional modes have been observed in the excitation spectra of jet-cooled magnesium tetraphenylporphin[18] and triptycene.[19] With an atom–atom type calculation using an 6-exp-1 potential,[20] a calculation of the librational potential was performed.[21] This calculation led to a molecular conformation of binaphthyl where the rings were nearly orthogonal (2° to the *cis* side) and led to a librational frequency of 28 cm^{-1} using an interconnecting C–C' bond lenght of 1.498 Å.[14] On deuteration this frequency dropped to 27 cm^{-1}. For the *B* symmetry dimer states an appreciable drop in librational frequency on deuteration is indeed noted. For the lowest *A* type progression no deuteration effect on the librational frequency is found. This indicates the subtleties of the potential energy surface of the different states in the molecule. A further significant outcome of the calculation was that the librational frequency was little dependent on the C–H distance but rather sensitive to a change in the interconnecting C–C' bond. For changes in the C–C' bond length near 1.5 Å, a change in librational frequency of $-4.3\ cm^{-1}/0.1$ Å was calculated. While we recognize the fact that this calculation should be only applicable to a prediction of the torsional modes on the ground state surface, the outcome can certainly be used to support the assignment of these low frequency modes to torsional modes of the molecule.

The second aspect of interest concerns the intensity distribution among the members of the librational progression. First we note that this intensity distribution is different for the different dimer transitions, which implies that the excited state potential for these states has a minimum at different interplanar angles. Second we remark that the torsional motion in BN is of *A* symmetry which leads to the possible observation of odd and even quanta in the spectrum. Finally we note again that the intensity distribution in the librational progression is rather dependent on vibrational excitation, which indicates that the electronic potential energy surface in the excited state is extremely sensitive to the coupling between the vibronic excitations. This notion supports the idea of a low barrier between the different conformations.

Using a simple model of a one dimensional harmonic oscillator for the torsional motion, with identical force constant in the ground and excited states, we can calculate from the Franck–Condon envelope in each librational progression the rotational displacement or, in other words, the change of the interplanar angle on optical excitation in BN.

The intensity distribution among the members of the torsional progression is given for this case by the expression[22]:

$$I_{0-n}/I_{0-0} = (\tfrac{1}{2}\alpha^2)^n/n!\,, \tag{2}$$

where I_{0-n}/I_{0-0} is the relative intensity of the *n*th librational member in the progression compared to the origin. α is a dimensionless constant $\alpha = \phi/\phi_0$ where ϕ is the rotational displacement on excitation and $\phi_0 = (\hbar/\pi I \nu_0)^{1/2}$. I is the reduced moment of inertia for the torsional motion. For the conformation of BN in which the naphthalene rings are perpendicular to one another, I is calculated to be 4.2×10^{-45} kg^2. Using for ν_0 an average value of 29 cm^{-1} (for BN-h_{14}) we calculate $\phi_0 = 5.5°$. Using this simple model we have tried to fit the Franck–Condon envelope of the four librational progressions in the origin region. For O_1 we obtain $\alpha \approx 1.8$, for O_2, $\alpha \approx 2.2$, for O_3, $\alpha \approx 1$ and finally for O_4, $\alpha \leqslant \frac{1}{2}$. There are several things to note. First it is observed that for the lower two dimer components (ascribed to the *trans* conformation by us) α is large but not identical for the *A* and *B* states. For the upper dimer levels, assigned to the *cis* conformation, α is smaller but also different for the two dimer levels. The fact that α is much larger for the lower two dimer levels than for the upper ones was used to decide which two progressions arise from the same conformation. The fact that α is different for dimer levels arising from the same conformation is a remarkable point, the implication being that in the *A* and *B* dimer states of the same conformation the interplanar angle is different. Apparently the interaction between the naphthalene molecules in BN is of the same order as the barrier height between the conformations, resulting in a separate potential energy surface for the *A* and *B* levels. This observation led to assigning a possible different Φ for the dimer states in Eq. (1). Finally, it is noted that for the librational progression starting at the *B* level at 31 716 cm^{-1}, with α chosen such that it fits the intensity of the first three members in the progression, one does not predict as abrupt a collapse in intensity of the higher quanta as is observed. This anomaly could be due to an increased radiationless rate for these higher torsional overtones resulting in an underestimate of their intensity in the excitation spectrum. Such an effect is to be expected of course when these torsional overtones approach the barrier.

We end this discussion of the origin librational progressions by pointing out that the angular change for absorption to the *B* potential energy surface in the *trans* conformation is 12° and in the *cis* form 6°. As the optical spectrum shows no evidence of level crossing, meaning that the second excited state of BN has become the lower one in any conformation, we conclude from the calculations by Post *et al.*[13] and Bigelow and Anderson[23] that the ground state conformation indeed must be *cis* and the interplanar angle close to 90°. With an interplanar angle of say 88° we calculate that, in the excited state for the *B* potential energy surface, the *cis* conformation is at 82° and the *trans* at 100°.

A rough estimate of the barrier height on the *B*-symmetric potential is obtained by positioning the calculated librational potentials at the inferred torsional angles. In this

way we find a barrier of $\sim 100\ cm^{-1}$, which indeed is very low and would explain the observed anomaly of the librational Franck–Condon contour discussed above.

For the potential energy surface of A symmetry the corresponding angles in the excited state are $\sim 85°$ and 98°. With these interplanar angles we can also calculate the magnitude of γ from the relative intensity of the A and B dimer levels in the *cis* and *trans* conformation and the help of Eq. (1). It is found that good agreement with the data can be obtained for $\gamma \approx 1.2$. In fact this value of γ is rather insensitive to a choice of interplanar angle in the ground state.

A final point of interest involving the torsional motion of BN relates to the observation that, when the BN molecule undergoes a torsional motion around the C–C' bond, the moment of inertia for this motion changes. In fact during such a (classical) torsional motion the two principal axes for rotation of the molecule perpendicular to the C_2 axis wobble in a plane perpendicular to the C_2 axis. This implies a strong coupling between the torsional motion of the molecule and molecular rotations around the axes perpendicular to the C_2 axis. This fact will be of great significance in the discussion of the emission spectra of BN which are dealt with in the next section.

D. Emission spectra

Recently Riley *et al.*[8] succeeded in obtaining highly resolved vibronic emission spectra at 4.2 K of BN frozen in a *n*-pentane Shpol'skii matrix. Two quite different emission spectra were observed. One of the spectra looked very naphthalene-like, with a weak origin at 31 767 cm^{-1} while the other was spectrally very different with a strong origin at 26 917 cm^{-1}. Note that the origin of the naphthalene-like emission spectrum is very close to the "origins" we observed in the jet-cooled BN molecule. These observations were interpreted by Riley *et al.*[8] by assuming that there were two BN species in the matrix, one with the naphthalene rings (nearly) perpendicular and the other with a more planar conformation. As was shown in the previous sections, in the gas phase the excited molecule also adopts two conformations but the transition energies are nearly the same. In the following discussion we will show that the observations made by Riley *et al.*[8] are very pertinent to the discussion of the molecular dynamics that occur after optical excitation of the isolated BN molecule. In Fig. 6 we show the emission spectra of BN after exciting the molecule to states with different amounts of excess vibrational energy. There are several things to note. The first one is that, irrespective of the amount of excess vibrational energy, the origin in emission remains at the same position. The only noticeable feature is a broadening of the spectrum with increased excess vibrational energy. In fact, as remarked in our previous letter on this subject,[9] the spectrum looks, except for its broadness, very much like the naphthalene-like BN emission observed in a *n*-pentane matrix at low temperature. A more precise position of the origin, than previously reported[9] was obtained by exciting the molecule into the intense dimer origin at 31 737 cm^{-1} with an excimer-pumped dye laser. A representative emission spectrum arising from the vibrationally cold molecule is shown in Fig. 7. From this spectrum we conclude that the most intense line in the emission spectrum occurs at

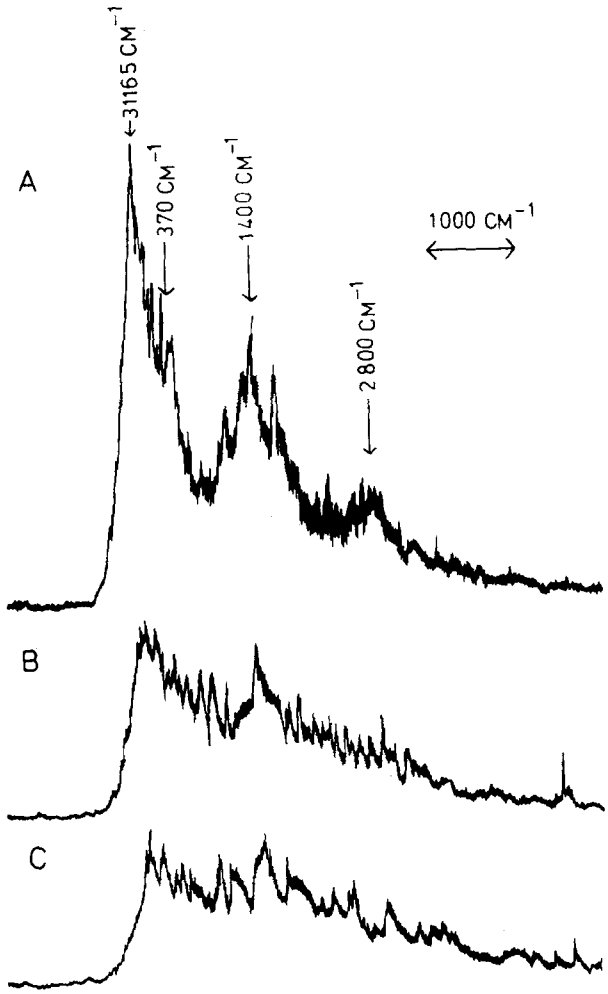

FIG. 6. Emission spectra of 1,1'-binaphthyl-h_{14} in a jet after excitation to states with different amount of excess vibrational energy. In (A) the excess vibrational energy, with respect to O_1, is about 460 cm^{-1}, in (B) 940 cm^{-1} and in (C) 1570 cm^{-1}. The spectra were taken with a spectral resolution of 100 cm^{-1}. An increase in resolution did not change the band shapes which indicates that the observed band widths are intrinsic.

31 165 ± 20 cm^{-1}. The interval between this intense line and the transition excited is then calculated to be 572 ± 25 cm^{-1}. Other peaks in the emission spectrum have been identified at 370, 1400, and 2800 (all ± 50 cm^{-1}) from the position of the false origin. In fact, the overall Franck–Condon envelope of the spectrum and the vibrational intervals, are so

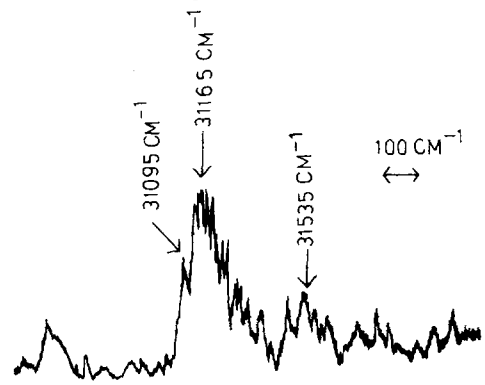

FIG. 7. Emission spectrum of 1,1'-binaphthyl-h_{14} in a jet after excitation into the O_3 origin at 31 737 cm^{-1}. Note the change in scale compared to Fig. 6. The arrow in the spectrum indicates the position of a shoulder in the emission spectrum which was also seen in a consecutive run. Spectral resolution in this scan was 100 cm^{-1}. The most red-shifted peak in the spectrum is stray light at the excitation wavelength.

similar to those observed for one of the emitting BN species in *n*-pentane, that we assign the emission spectra of Figs. 6 and 7 to emission of vibrationally cold BN molecules. The 572 cm^{-1} mode observed in emission then should be the b_{1g} type analog of the 390 cm^{-1} coupling mode observed in absorption. Similarly the 940 cm^{-1} mode in emission must then be correlated with a 788 cm^{-1} mode observed in absorption. The 1400 and 2800 cm^{-1} vibrational additions on the false origin correspond to one and two quanta excitations of $a \sim 1400$ cm^{-1} totally symmetric mode, which in the *n*-pentane matrix was found to be 1391 cm^{-1}. The only problem with this analysis is that the vibrational frequency of 572 cm^{-1} for the ground state "b_{1g} type" mode in BN seems too high, especially when compared with the value of 513 cm^{-1} obtained for this mode for one of the emitting BN species in *n*-pentane. It therefore seems attractive to consider the possibility of an interconversion from the *cis-B* state to the *trans-A* level in BN after exciting into the strong origin at 31 737 cm^{-1}. If the BN species excited at this frequency converts to the one with its origin at 31 666 cm^{-1} one calculates a vibrational interval of 501 $\pm$ 25 cm^{-1} which is close in frequency to the 513 cm^{-1} observed for BN in *n*-pentane. In the high resolution emission spectra (see Fig. 7), there seems to be an indication of a shoulder $\sim$70 cm^{-1} to the red of the most intense false origin. This shoulder then might correspond to the false origin of the *unrelaxed* emission from the excited species. This point, however, needs further study and could not be addressed with the present dye laser equipment available. Irrespective of this important detail there is just no question as to the naphthalenic character of the emission observed after excitation of BN. This observation sharply contrasts with the situation occurring in a solution of BN where, after excitation, the emission is red shifted and is not at all reminiscent to naphthalene. The conclusion, therefore, must be that in the gas phase, after vibronic excitation, a very efficient conversion of vibrational into librational energy occurs with the possible energy mismatch taken up by the molecular rotations. In the preceeding section it was explained why in BN a strong coupling occurs between the torsional mode and molecular rotations perpendicular to the C_2 axis. Let us now continue with the interpretation of the emission characteristics using the premise of a fast internal conversion process involving torsional modes. This concept easily explains the large width of the vibrational transitions after exciting the molecule to a state with excess vibrational energy. The 700 cm^{-1} width observed after exciting BN into the false origin at 32 122 cm^{-1} in this picture results from the Franck–Condon contour of the emission of librationally very hot molecules ($\sim$20 quanta) to a librationally hot ground state surface. After the emission process the molecule is thus left librationally hot. When the amount of excess vibrational energy is increased the same process occurs so that the emission becomes smeared out through anharmonicity effects in the librational manifold.

This idea is confirmed by looking at the line shape of the false origin after excitation in the vibrationally cold origin at 31 737 cm^{-1}. Figure 7 shows this line shape under the highest possible resolution. The first observation is that the vibronic line shape has become much sharper. Taking into account a spectral resolution of 100 cm^{-1} we estimate the intrinsic width of this "transition" to be 100 cm^{-1}. Figure 7 further shows that the transition is asymmetric with the low-energy side falling off much slower than the high energy side. This is in agreement with what we expect to observe when the librational contour in emission is similar to that observed in absorption. We therefore conclude that the width in emission of the vibronic transitions are indeed due to librational Franck–Condon contours.

We finally wish to discuss the observed fluorescence lifetimes as a function of excess vibrational energy. In the region of the origin we measure, for the strong lines, fluorescence lifetimes of 60 $\pm$ 5 ns. In the false origin the lifetime is measured to be 50 $\pm$ 5 ns and this trend continues: at 1500 cm^{-1} excess vibrational energy the lifetime is reduced to 30 $\pm$ 5 ns. The first noteworthy thing is that the fluorescence lifetime after excitation in the most intense origin is found to be close to the lifetime measured for BN in frozen solution. This fits into the picture that the emitting state in the gas phase is a naphthalenic state. The decrease in fluorescence lifetime with an increase in vibrational energy must be due to an increase in the rate constant for radiationless deactivation, a feature also observed for naphthalene.[15] It would be interesting to measure accurately the fluorescence lifetimes of all the states in the origin for both perproto and perdeutero BN, especially with regard to the question of interconversion between the different BN conformations. This is planned in a future study of BN after the installment of a more powerful dye laser system than the one presently available.

A final comment concerning the dynamics of the internal conversion process must be made on the basis of a measurement of a high-resolution scan of the most intense line in the spectrum at 32 122 cm^{-1}. Such a scan of the excitation profile showed that the linewidth of this transition was less than 0.6 cm^{-1}, implying that the intramolecular relaxation process occurs on a timescale of at least 10 ps. Such high resolution scans are also planned for other lines in the spectrum for both isotopes.

IV. SUMMARY AND CONCLUSION

From a spectroscopic study of 1,1'-binaphthyl in a free jet we have learned the following. First we have shown that the lowest excited state potential in 1,1'-binaphthyl exhibits a double minimum potential along the torsional coordinate and that this potential energy surface is possibly different for the states of gerade and ungerade symmetry. The barrier between the two conformations is lower than 200 cm^{-1} and may be as low as 100 cm^{-1}. Second we have shown that a dimer description of the binaphthyl state provides a useful picture of the nature of the lowest excited states and that the transition dipole in the naphthalene subunit is aligned in the plane at an angle of 50° with respect to the naphthalene long axis. We have further shown that very efficient intramolecular vibrational relaxation occurs through conversion of excess vibrational energy into librations. In this process molecular rotations play a dominant role in providing the matching energy. Binaphthyl thus behaves not only like a "mini exciton" but also as a "mini crystal" in the sense that

the emission spectrum always comes from the vibrationally relaxed molecule. The torsional mode and the molecular rotations in this system form the heat bath. We have also provided evidence, not conclusive so far, that after excitation of the binaphthyl conformer at higher energy emission comes from the lowest one. If confirmed, the situation would be very similar to the one proposed to occur in liquid solutions of binaphthyl, where supposedly after excitation of one conformation, emission from the energetically lower one occurs. In any case the main question to be answered is why in gaseous 1,1'-binaphthyl the different conformations have nearly equal excitation energies, while in solution this difference is on the order of 4000 cm^{-1}. The answer must be that solvation greatly affects the potential for rotation around the connecting C–C' bond. This is understandable if one realizes that the potential for this torsional motion in the free molecule is extremely flat, enabling the formation of a complex of BN with a solute molecule with a structure of the BN species which is quite different from the structure of the isolated molecule.

Several questions concerning the dynamics of the molecule remain. The most important one is whether or not the different binaphthyl conformations in free space can be interconverted by optical excitation in vibrationless dimer states other than the energetically lowest one. We intend to further study this aspect by exciting the molecule with a more powerful dye-laser system than was available at the time of the experiments. Furthermore it seems useful to make a systematic study of the lifetimes of all librational levels in the region of the origin in order to obtain more quantitative information on the barrier heights. An interesting test of the model proposed seems to be to study the spectrum of 1-(1'-naphthyl-d_7)-naphthalene-h_7 in a jet. In particular, knowledge of the position of the naphthalene "monomer" in BN-h_{14} and BN-d_{14} would be revealing. Several other interesting experiments are suggested by the results of this study. First it seems that 9,9'-bianthryl should behave analogous to 1,1'-binaphthyl except that the "dimer" splitting could be much larger. Study of this sytems seems worthwhile. Even more interesting might be a study of the molecule 9-(1-naphthyl)-anthracene in a jet. The results obtained in this paper suggest that very efficient energy transfer might occur from the naphthalene to the anthracene chromophore with the torsional mode acting as the accepting mode for the excess energy in this "mini-mixed crystal." It might also be worthwhile to engage in a high-resolution optical study of BN in a skimmed jet,[24] to expose the predicted strong coupling between rotational and torsional modes in this molecule. Finally, optical study of biaryls in the gas phase is important to understanding of the dynamics of the torsional isomerization of these molecules in solution.[25] It is hoped that from such studies detailed knowledge about the intramolecular torsional potential will be obtained. Such information is crucial in a molecular dynamics simulation of this simple one-dimensional photochemical reaction.

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